

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 004 241 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
31.05.2000 Bulletin 2000/22

(21) Application number: 99309154.5

(22) Date of filing: 17.11.1999

(51) Int Cl.7: **A01N 47/38**, A01N 43/824,
C07D 271/10, C07D 271/12,
C07D 413/04, C07D 417/04

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 23.11.1998 US 197969

(71) Applicant: **American Cyanamid Company**
Madison, New Jersey 07940-0874 (US)

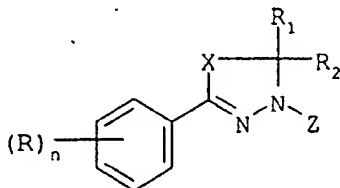
(72) Inventors:
• **Takasugi, James Jan**
Lawrenceville, New Jersey 08648 (US)
• **Buckwalter, Brian Lee**
Yardley, Pennsylvania 19067 (US)

(74) Representative: **Connelly, Michael John et al**
c/o Patent Department
Wyeth Laboratories
Huntercombe Lane South
Taplow
Maidenhead Berkshire SL6 0PH (GB)

(54) **2-Aryl-Delta2-1,3,4- (oxa and thia)diazoline insecticidal and acaricidal agents**

(57) The present invention relates to 2-aryl- Δ^2 -1,3,4-(oxa and thia)diazoline compounds having the structural formula

and compositions and methods comprising those compounds for the control of insect and acarid pests.



EP 1 004 241 A1

Description

BACKGROUND OF THE INVENTION

[0001] Insect and acarid pests destroy growing and harvested crops. In the United States, agronomic crops must compete with thousands of those pests. In particular, tobacco budworms and southern armyworms are especially devastating to crops.

[0002] Tobacco budworms -cause tremendous economic losses in agronomic crops. In particular, budworms devastate cotton crops by feeding on green bolls. Control of budworms is complicated by their resistance to many common insecticides, including organophosphates, carbamates and pyrethroids.

[0003] In spite of the commercial insecticides and acaricides available today, damage to crops, both growing and harvested, caused by insect and acarid pests still occurs. Accordingly, there is ongoing research to create new and more effective insecticidal and acaricidal agents.

[0004] Certain N-carbamoyl-3-carboxyaryl-heterocyclic and hydrazinecarboximidamido-hydrazone compounds which are useful as herbicidal agents are described in U.S. 5,670,456. However, that patent does not describe any insecticidal or acaricidal activity.

[0005] Certain cyclic 1,3,4-oxadiazoline compounds are described by D. Kochetov et al in *Ukrainskii Khimicheskii Zhurnal*, 57(2), pp. 215-217 (1991). However, D. Kochetov et al do not disclose any utility for their cyclic 1,3,4-oxadiazoline compounds

[0006] It is, therefore, an object of the present invention to provide compounds which are useful for the control of insect and acarid pests.

[0007] It is also an object of the present invention to provide a method for the control of insect and acarid pests.

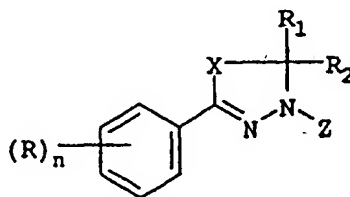
[0008] It is a further object of this invention to provide a method for the protection of growing and harvested crops from damage caused by insect and acarid attack and infestation.

[0009] These and other objects of the present invention will become more apparent from the description thereof set forth below.

SUMMARY OF THE INVENTION

[0010] The present invention comprises 2-aryl- Δ^2 -1,3,4-(oxa and thia)diazoline compounds which are useful for the control of insect and acarid pests. Those compounds are also useful for protecting plants from damage caused by insect and acarid attack and infestation.

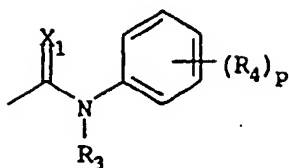
[0011] The pesticidal 2-aryl- Δ^2 -1,3,4-(oxa and thia)-diazoline compounds of the present invention have the structural formula I



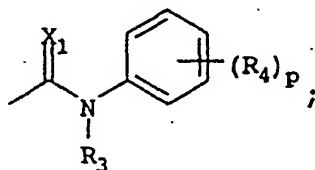
(I)

wherein

X is O or S(O)_m;
Z is



$C(X_1)R_5$, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl,
 benzyl optionally substituted on the phenyl ring with any combination of from one to three halogen, C_1 - C_6 alkyl,
 C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio groups, or
 phenyl optionally substituted with any combination of from one to three halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl,
 C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio groups,
 provided that when X is O, Z is



n and p are each independently 0, 1, 2 or 3;

X_1 is O or S;

R and R_4 are each independently halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, OR_6 , $S(O)_qR_7$, nitro, cyano, NR_8R_9 ,
 CO_2R_{10} , $C(O)R_{11}$ or phenyl optionally substituted with any combination of from one to three halogen, C_1 - C_6 alkyl,
 C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio groups, or
 two adjacent R groups or R_4 groups may be taken together to form a ring wherein RR or R_4R_4 is represented
 by: $-OCH_2O-$, $-OCF_2O-$ or $-CH=CH-CH=CH-$;

R_6 and R_7 are each independently hydrogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl or

phenyl optionally substituted with any combination of from one to three halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl,
 C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio groups;

R_8 , R_9 , R_{13} and R_{14} are each independently hydrogen, C_1 - C_6 alkyl, C_1 - C_6 alkylcarbonyl or

phenyl optionally substituted with any combination of from one to three halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl,
 C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio groups;

R_{10} and R_{11} are each independently hydrogen, C_1 - C_6 alkyl or C_1 - C_6 haloalkyl;

R_1 and R_2 are each independently hydrogen, C_3 - C_7 cycloalkyl, C_1 - C_6 haloalkyl, C_3 - C_6 alkenyl, C_3 - C_6 haloalkenyl,
 C_3 - C_6 alkynyl, C_3 - C_6 haloalkynyl, C_2 - C_6 alkoxyalkyl, $(CH_2)_vC(O)R_{12}$, C_1 - C_6 alkyl optionally substituted with one phe-
 noxy or phenyl group wherein the phenyl ring of each group is independently, optionally substituted with from one
 to three halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio
 groups,

phenyl optionally substituted with from one to three halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 -
 C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio groups, or

a 5- or 6-membered heteroaromatic ring optionally substituted with any combination of from one to three
 halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio groups,
 and when R_1 and R_2 are taken together with the atom to which they are attached they may form a C_3 - C_6 cycloalkyl
 ring wherein R_1R_2 is represented by: $-(CH_2)_t-$ where t is 2, 3, 4 or 5;

m, q and v are each independently 0, 1 or 2;

R_{12} is hydrogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio or
 $NR_{13}R_{14}$;

R_3 is hydrogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl or $C(O)R_{15}$;

R_{15} is C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy or C_1 - C_6 haloalkoxy; and

R_5 is C_1 - C_6 alkyl,

phenyl optionally substituted with any combination of from one to three halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl,
 C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio groups, or

benzyl optionally substituted on the phenyl ring with any combination of from one to three halogen, C_1 - C_6 alkyl,
 C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio or C_1 - C_6 haloalkylthio groups; and

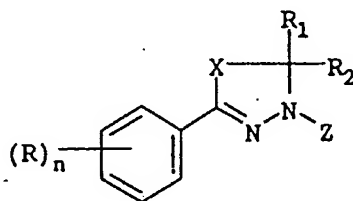
the optical isomers thereof and the agriculturally acceptable salts thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The present invention provides a method for the control of insect or acarid pests which comprises contacting said pests or their food supply, habitat or breeding grounds with a pesticidally effective amount of a 2-aryl- Δ^2 -1,3,4-(oxa or thia)diazoline compound of formula I.

[0013] The present invention also provides a method for the protection of growing plants from attack or infestation by insect or acarid pests which comprises applying to the foliage of the plants, or to the soil or water in which they are growing, a pesticidally effective amount of a 2-aryl- Δ^2 -1,3,4-(oxa or thia)diazoline compound of formula I

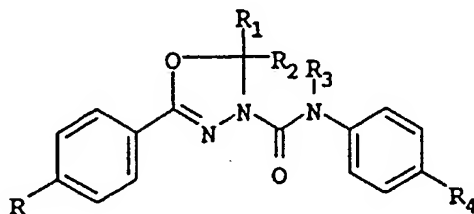
[0014] The pesticidal 2-aryl- Δ^2 -1,3,4-(oxa and thia)-diazoline compounds of the present invention have the structural formula I



(I)

wherein n, R, R₁, R₂, X and Z are as described hereinabove for formula I.

[0015] Preferred 2-aryl- Δ^2 -1,3,4-oxadiazoline compounds of the present invention are those having the structural formula II



(II)

wherein

R is halogen, C₁-C₄haloalkyl, C₁-C₄haloalkoxy or

phenoxy optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups;

R₄ is C₁-C₄haloalkyl, C₁-C₄haloalkoxy or C₁-C₄haloalkylthio;

R₁ is C₁-C₄alkyl;

R₂ is C₁-C₄alkyl, C₁-C₄haloalkyl, (CH₂)_vC(O)R₁₂ or 2-pyridyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups;

v is 0 or 1;

R₁₂ is C₁-C₄alkoxy or C₁-C₄haloalkoxy;

R₃ is hydrogen or C(O)R₁₅; and

R₁₅ is C₁-C₄alkoxy.

[0016] More preferred insecticidal and acaricidal agents of the present invention are those having the structural formula II wherein

R is F, Br, Cl or phenoxy;
 R₄ is CF₃, OCF₃ or SCF₃;
 R₁ is CH₃;
 R₂ is CH₃, CH₂Cl, CH₂CF₃, CF₃, CH₂CO₂CH₃ or 2-pyridyl; and
 R₃ is hydrogen or CO₂CH₃.

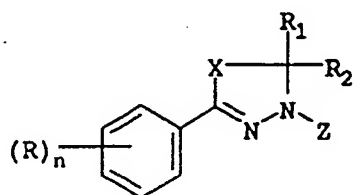
[0017] Compounds of this invention which are particularly effective insecticidal agents include

2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-bromophenyl)-5,5-dimethyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-fluorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 5,5-dimethyl-2-(*p*-phenoxyphenyl)-4'-[(trifluoromethyl)-thio]-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-4'-(trifluoromethoxy)-5-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-chlorophenyl)-5-methyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 4,5-bis(trifluoromethyl)-2-(*p*-fluorophenyl)-5-methyl-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-fluorophenyl)-5-methyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-fluorophenyl)-5-methyl-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-bromophenyl)-5-(chloromethyl)-5-methyl-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 methyl N-[[2-(*p*-chlorophenyl)-5,5-dimethyl-Δ²-1,3,4-oxadiazolin-4-yl]carbonyl]-*p*-(trifluoromethoxy)-carbanilate;
 methyl N-[[2-(*p*-chlorophenyl)-5,5-dimethyl-Δ²-1,3,4-oxadiazolin-4-yl]carbonyl]-*p*-(trifluoromethyl)-carbanilate;
 and
 methyl 2-(*p*-chlorophenyl)-5-methyl-4-[[*p*-(trifluoromethoxy)phenyl]carbamoyl]-Δ²-1,3,4-oxadiazoline-5-acetate,
 among others.

[0018] In formula I above, 5- and 6-membered heteroaromatic rings include, but are not limited to, pyridyl, pyrazolyl, imidazolyl, triazolyl, isoxazolyl, tetrazolyl, pyrazinyl, pyridazinyl, triazinyl, furanyl, thienyl, and thiazolyl rings each optionally substituted as described in formula I above.

[0019] Exemplary of halogen hereinabove are fluorine, chlorine, bromine and iodine. The terms "C₁-C₆haloalkyl", "C₁-C₄haloalkyl", "C₁-C₆haloalkoxy", "C₁-C₄haloalkoxy", "C₁-C₆haloalkylthio" and "C₁-C₄haloalkylthio" are defined as a C₁-C₆alkyl group, a C₁-C₄alkyl group, a C₁-C₆alkoxy group, a C₁-C₄alkoxy group, a C₁-C₆alkylthio group and a C₁-C₄alkylthio group substituted with one or more halogen atoms, respectively.

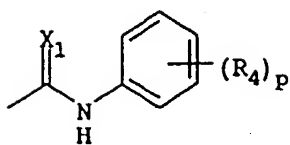
[0020] Novel 2-aryl-Δ²-1,3,4-(oxa and thia)diazoline compounds of the present invention are those having the structural formula I



(I)

wherein n, R, R₁, R₂, X and Z are as described hereinabove, provided that: (1) R is other than CO₂R₁₀ when R is on the ortho-position of the phenyl ring, and (2) R₂ is other than ethyl or unsubstituted phenyl when X is O, n and p are 0 and R₁ is methyl.

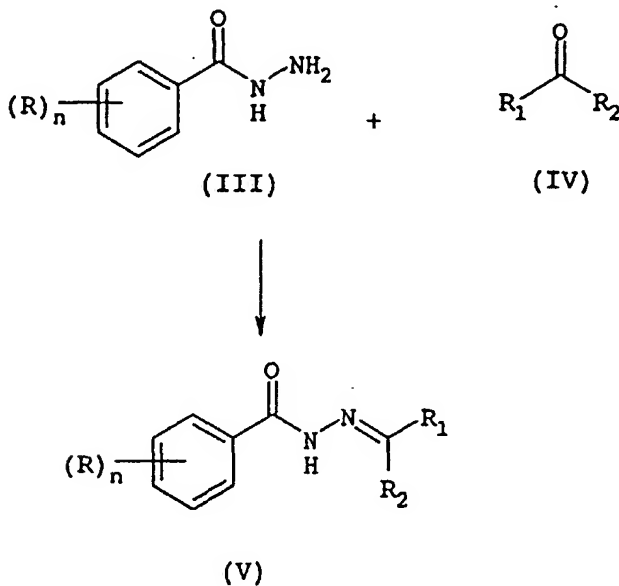
[0021] Formula I compounds wherein X is O and Z is

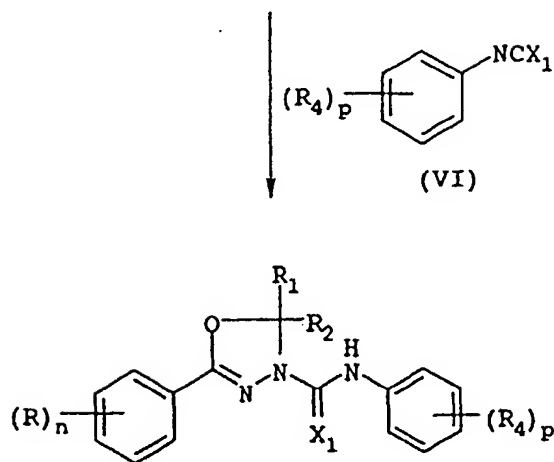


10 may be prepared, as illustrated in Flow Diagram I, by reacting a hydrazine of formula III with a ketone of formula IV in the presence of a solvent such as acetone, ethanol, methylene chloride, 1,1-diethoxyethane and the like, preferably at an elevated temperature, to form a hydrazone of formula V, and reacting the formula V hydrazone with an isocyanate or isothiocyanate of formula VI in the presence of a solvent such as 1,2-dichloroethane and ethyl acetate, preferably at an elevated temperature.

15

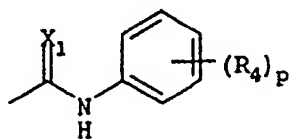
FLOW DIAGRAM I



FLOW DIAGRAM I (cont.)

[0022] Alternatively, formula I compounds wherein X is O, R₁ is methyl, R₂ is C₁-C₆haloalkyl and Z is

25



may be prepared, as shown in Flow Diagram II, by reacting a hydrazine of formula III with a 1-haloalkyl-1-acetoxyethylene compound of formula VII in the presence of a solvent such as ethanol, preferably at an elevated temperature, to obtain a hydrazone of formula VIII, and reacting the formula VIII hydrazone with an isocyanate or isothiocyanate of formula VI in the presence of a solvent such as 1,2-dichloroethane and ethyl acetate, preferably at an elevated temperature.

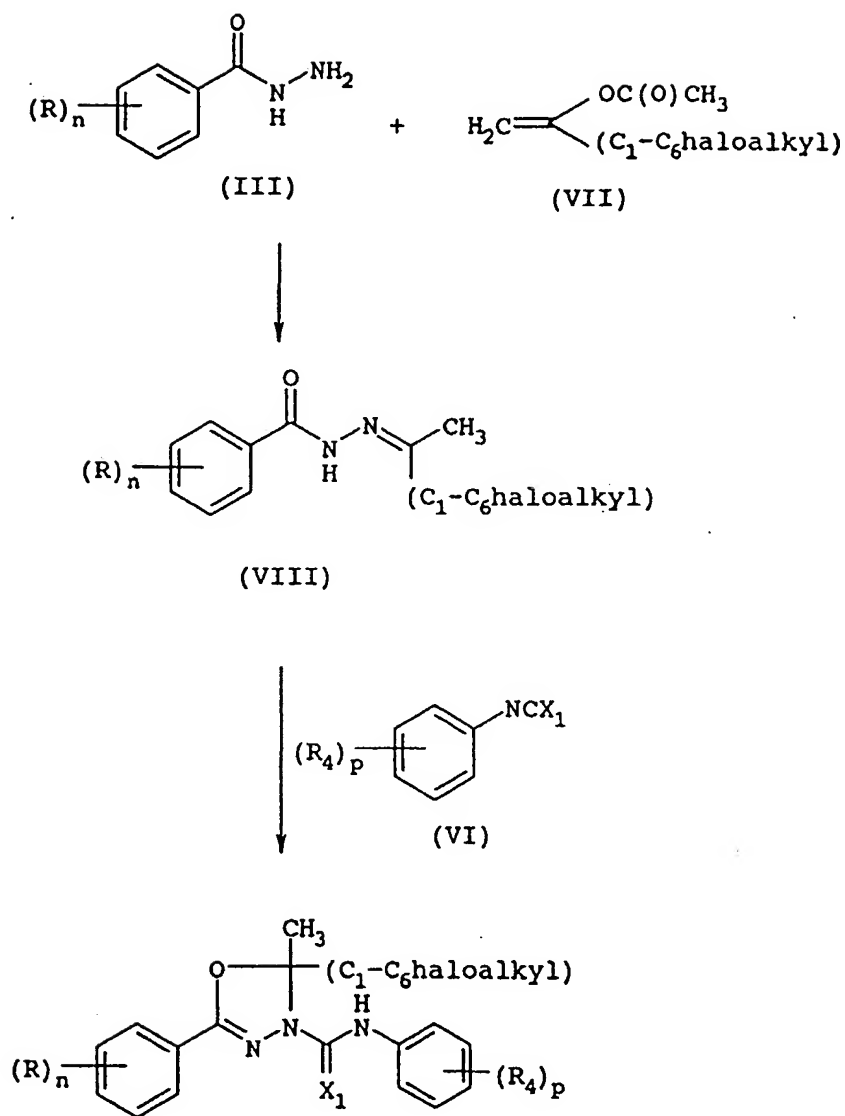
35

40

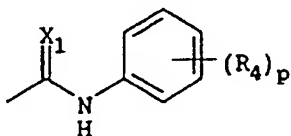
45

50

55

FLOW DIAGRAM II

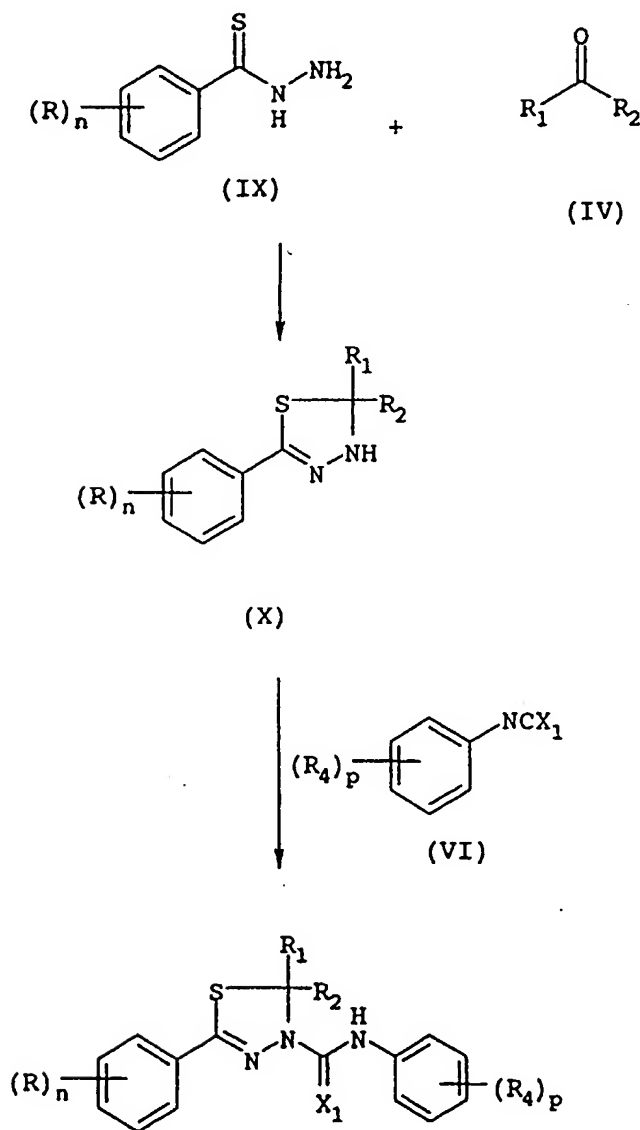
[0023] Formula I compounds wherein X is S and Z is



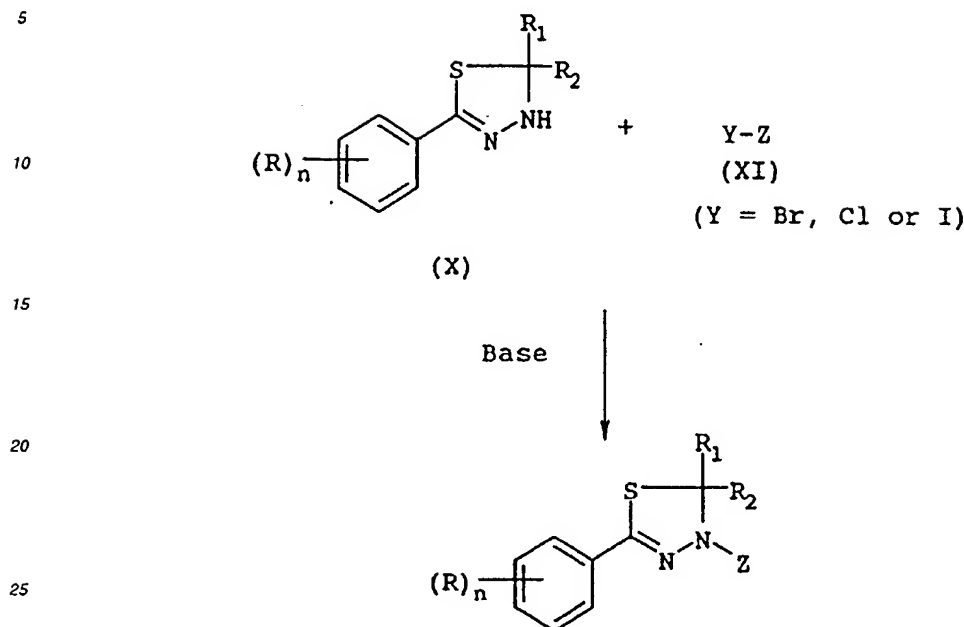
may be prepared, as illustrated in Flow Diagram III, by reacting a hydrazine of formula IX with a ketone of formula IV

in the presence of a solvent such as acetone, ethanol, methylene chloride, 1,1-diethoxyethane and the like to form a 2-aryl- Δ^2 -1,3,4-thiadiazoline of formula X, and reacting the formula X compound with an isocyanate or isothiocyanate of formula VI in the presence of a solvent such as 1,2-dichloroethane and ethyl acetate.

FLOW DIAGRAM III



[0024] Formula I compounds wherein X is S and Z is $C(X_1)R_5$, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, optionally substituted benzyl or optionally substituted phenyl may be prepared, as illustrated in Flow Diagram IV, by reacting a 2-aryl- Δ^2 -1,3,4-thiadiazoline of formula X with a halide compound of formula XI and a base in the presence of a solvent.

FLOW DIAGRAM IV

[0025] In addition, certain compounds of formula I may be converted into other compounds of formula I by using conventional procedures known to those skilled in the art.

[0026] The 2-aryl- Δ^2 -1,3,4-(oxa and thia)diazoline compounds of the present invention are effective for controlling insect and acarid pests. Those compounds are also effective for protecting growing or harvested crops from damage caused by insect and acarid attack and infestation.

[0027] Insects controlled by the a 2-aryl- Δ^2 -1,3,4-(oxa and thia)diazoline compounds of this invention include Lepidoptera such as tobacco budworms, cabbage loopers, cotton boll worms, beet armyworms, southern armyworms and diamondback moths; Homoptera such as aphids, leaf hoppers, plant hoppers and white flies; Thysanoptera such as thrips; Coleoptera such as boll weevils, Colorado potato beetles, southern corn rootworms, western corn rootworms and mustard beetles; and Orthoptera such as locusts, crickets, grasshoppers and cockroaches. Acarina controlled by the compounds of this invention include mites such as two-spotted spider mites, carmine spider mites, banks grass mites, strawberry mites, citrus rust mites and leprosis mites.

[0028] In practice generally about 10 ppm to about 10,000 ppm and preferably about 100 ppm to about 5,000 ppm of a formula I compound, dispersed in water or another liquid carrier, is effective when applied to plants or the soil in which the plants are growing to protect the plants from insect and acarid attack and infestation.

[0029] The 2-aryl- Δ^2 -1,3,4-(oxa and thia)diazoline compounds of this invention are also effective for controlling insect and acarid pests when applied to the foliage of plants and/or to the soil or water in which said plants are growing in sufficient amount to provide a rate of about 0.1 kg/ha to 4.0 kg/ha of active ingredient.

[0030] While the compounds of this invention are effective for controlling insect and acarid pests when employed alone, they may also be used in combination with other biological agents, including other insecticides and acaricides. For example, the formula I compounds of this invention may be used effectively in conjunction or combination with pyrethroids, phosphates, carbamates, cyclodienes, endotoxin of *Bacillus thuringiensis* (Bt), formamidines, phenol tin compounds, chlorinated hydrocarbons, benzoylphenylureas, pyrroles and the like.

[0031] The compounds of this invention may be formulated as emulsifiable concentrates, flowable concentrates or wettable powders which are diluted with water or other suitable polar solvent, generally *in situ*, and then applied as a dilute spray. Said compounds may also be formulated in dry compacted granules, granular formulations, dusts, dust concentrates, suspension concentrates, microemulsions and the like all of which lend themselves to seed, soil, water and/or foliage applications to provide the requisite plant protection. Such formulations or compositions of the present invention include a compound of the invention (or combinations thereof) admixed with one or more agronomically acceptable inert, solid or liquid carriers. Those compositions contain a pesticidally effective amount of said compound

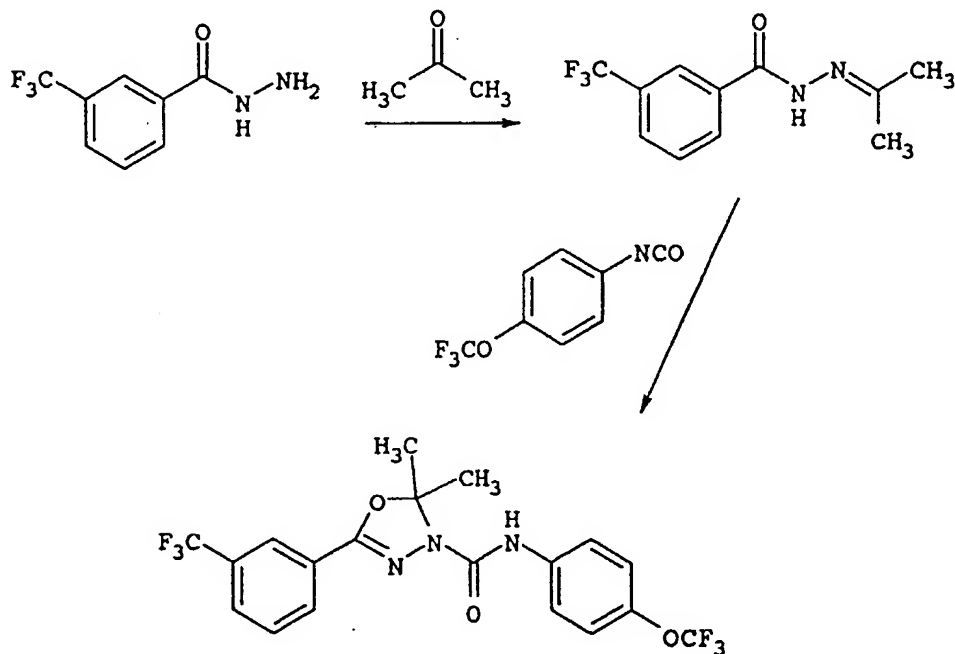
or compounds, which amount may vary depending upon the particular compound, target pest, and method of use. Those skilled in the art can readily determine what is a pesticidally effective amount without undue experimentation.

[0032] In order to facilitate a further understanding of the invention, the following examples are presented primarily for the purpose of illustrating more specific details thereof. The scope of the invention should not be deemed limited by the examples, but encompasses the entire subject matter defined in the claims.

EXAMPLE 1

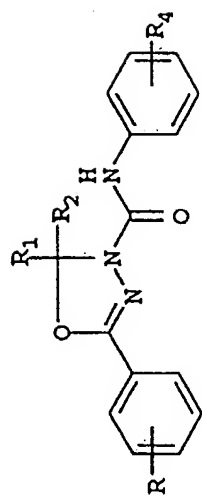
Preparation of 2-(α,α,α -Trifluoro-*m*-tolyl)-5,5-dimethyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide

[0033]



[0034] A solution of *m*-trifluoromethylbenzoyl hydrazine (1.84 g) and acetone (40 mL) is refluxed for 48 hours, cooled to room temperature and concentrated *in vacuo* to obtain a colorless hydrazone (1.48 g, m.p. 100-103°C). A solution of the hydrazone (0.74 g), *p*-trifluoromethoxyphenylisocyanate (0.62 g), and 1,2-dichloroethane (15 mL) is refluxed for 16 hours, cooled to room temperature, and concentrated *in vacuo* to give the title product as a colorless solid (1.28 g, m.p. 120-122°C).

[0035] Using essentially the same procedure as described for the preparation of Example 1, but using the appropriately substituted hydrazine, ketone and isocyanate, the following compounds are obtained:



Example	R	R ₁	R ₂	R ₄	mp °C
2	4-Cl	CH ₃	CH ₃	4-OCF ₃	100-105
3	4-Cl	CH ₃	CH ₃	4-CF ₃	136-137
4	4-Cl	CH ₃	CH ₃	4-F	168-169
5	4-Cl	CH ₃	CH ₃	4-Cl	169-170
6	4-CF ₃	CH ₃	CH ₃	4-OCF ₃	121-122
7	4-CF ₃	CH ₃	CH ₃	4-CF ₃	136-137
8	3-CF ₃	CH ₃	CH ₃	4-CF ₃	156-158
9	4-Cl	CH ₃	CH ₃	4-SCF ₃	142-143
10	4-Cl	CH ₃	CH ₃	4-Br	
11	4-Cl	CH ₃	CH ₃	3-I	
12	4-Cl	CH ₃	CH ₃	4-I	
13	4-Cl	CH ₃	CH ₃	3-CF ₃	
14	4-Cl	CH ₃	CH ₃	4-CN	
15	4-Cl	CH ₃	CH ₃	3-CH ₃	



Example	R	R ₁	R ₂	R ₄	mp °C
16	4-Cl	CH ₃	CH ₃	4-CO ₂ C ₂ H ₅	
17	4-Cl	CH ₃	CH ₃	4-C ₆ H ₅	
18	4-Cl	CH ₃	CH ₃	2,5-di-CH ₃	
19	4-Cl	CH ₃	CH ₃	4-CH ₂ Cl	
20	4-Cl	CH ₃	CH ₃	3,5-di-CF ₃	
21	4-Cl	CH ₃	CH ₃	2,3-(CH=CHCH=CH)	
22	4-Cl	CH ₃	CH ₃	2,4-di-Cl	
23	2,4-di-F	CH ₃	CH ₃	4-Cl	
24	4-Cl	CH ₃	CH ₃	2,6-di-F	
25	4-Cl	CH ₃	CH ₃	3-Cl-4-F	
26	4-Cl	CH ₃	CH ₃	3,4-di-F	
27	4-Br	CH ₃	CH ₃	4-CF ₃	
28	4-F	CH ₃	CH ₃	4-CF ₃	
29	4-CH ₃	CH ₃	CH ₃	3-CF ₃	
30	4-OCH ₃	CH ₃	CH ₃	4-CF ₃	
31	4-C ₆ H ₅	CH ₃	CH ₃	4-CF ₃	
32	4-OC ₆ H ₅	CH ₃	CH ₃	4-CF ₃	
33	4-N(CH ₃) ₂	CH ₃	CH ₃	4-CF ₃	
34	4-I	CH ₃	CH ₃	4-CF ₃	
35	4-Br	CH ₃	CH ₃	4-OCF ₃	
36	4-F	CH ₃	CH ₃	4-OCF ₃	

Example	R	R ₁	R ₂	R ₄	mp °C
37	4-CH ₃	CH ₃	CH ₃	4-OCF ₃	
38	4-OCH ₃	CH ₃	CH ₃	4-OCF ₃	
39	4-C ₆ H ₅	CH ₃	CH ₃	4-OCF ₃	
40	4-OC ₆ H ₅	CH ₃	CH ₃	4-OCF ₃	
41	4-N(CH ₃) ₂	CH ₃	CH ₃	4-OCF ₃	
42	4-t-Butyl	CH ₃	CH ₃	4-OCF ₃	
43	4-I	CH ₃	CH ₃	4-OCF ₃	
44	H	CH ₃	CH ₃	4-CF ₃	
45	3,4-(CH=CHCH=CH)	CH ₃	CH ₃	4-CF ₃	
46	3,4-di-Cl	CH ₃	CH ₃	4-CF ₃	
47	4-NHC(O)CH ₃	CH ₃	CH ₃	4-CF ₃	
48	2,4-di-Cl	CH ₃	CH ₃	4-CF ₃	
49	H	CH ₃	CH ₃	4-OCF ₃	
50	3,4-di-Cl	CH ₃	CH ₃	4-OCF ₃	
51	3,4-(OCH ₂ O)	CH ₃	CH ₃	4-OCF ₃	
52	4-NHC(O)CH ₃	CH ₃	CH ₃	4-OCF ₃	
53	4-Cl	CH ₃	CH ₃	4-SCF ₃	
54	4-Cl	CH ₃	CH ₃	2-Cl	
55	4-Cl	CH ₃	CH ₃	3-SCH ₃	
56	4-Cl	CH ₃	CH ₃	2-OCF ₃	
57	4-Cl	CH ₃	CH ₃	2,4,6-tri-CH ₃	

Example	R	R ₁	R ₂	R ₄	mp °C
58	4-Cl	CH ₃	CH ₃	2,4,6-tri-Cl	
59	4-Br	CH ₃	CH ₃	4-I	
60	4-F	CH ₃	CH ₃	4-I	
61	4-CH ₃	CH ₃	CH ₃	4-I	
62	4-OCH ₃	CH ₃	CH ₃	4-I	
63	4-C ₆ H ₅	CH ₃	CH ₃	4-I	
64	4-OC ₆ H ₅	CH ₃	CH ₃	4-I	
65	4-N(CH ₃) ₂	CH ₃	CH ₃	4-I	
66	4-t-Butyl	CH ₃	CH ₃	4-I	
67	4-I	CH ₃	CH ₃	4-I	
68	4-Br	CH ₃	CH ₃	4-Br	
69	4-F	CH ₃	CH ₃	4-Br	
70	4-CH ₃	CH ₃	CH ₃	4-Br	
71	4-OCH ₃	CH ₃	CH ₃	4-Br	
72	4-NO ₂	CH ₃	CH ₃	4-Br	
73	4-C ₆ H ₅	CH ₃	CH ₃	4-Br	
74	4-OC ₆ H ₅	CH ₃	CH ₃	4-Br	
75	4-N(CH ₃) ₂	CH ₃	CH ₃	4-Br	
76	4-t-Butyl	CH ₃	CH ₃	4-Br	
77	4-I	CH ₃	CH ₃	4-Br	
78	4-Br	CH ₃	CH ₃	4-CN	

Example	R	R ₁	R ₂	R ₄	mp °C
79	4-F	CH ₃	CH ₃	4-CN	
80	4-CH ₃	CH ₃	CH ₃	4-CN	
81	4-OCH ₃	CH ₃	CH ₃	4-CN	
82	4-NO ₂	CH ₃	CH ₃	4-CN	
83	4-OC ₆ H ₅	CH ₃	CH ₃	4-CN	
84	4-N(CH ₃) ₂	CH ₃	CH ₃	4-CN	
85	4-I	CH ₃	CH ₃	4-CN	
86	4-Br	CH ₃	CH ₃	4-SCF ₃	
87	4-F	CH ₃	CH ₃	4-SCF ₃	
88	4-CH ₃	CH ₃	CH ₃	4-SCF ₃	
89	4-OCH ₃	CH ₃	CH ₃	4-SCF ₃	
90	4-NO ₂	CH ₃	CH ₃	4-SCF ₃	
91	4-C ₆ H ₅	CH ₃	CH ₃	4-SCF ₃	
92	4-OC ₆ H ₅	CH ₃	CH ₃	4-SCF ₃	
93	4-N(CH ₃) ₂	CH ₃	CH ₃	4-SCF ₃	
94	4-I	CH ₃	CH ₃	4-SCF ₃	
95	4-Cl	CH ₃	C ₆ H ₅	4-OCF ₃	52-62
96	4-Cl	CH ₃	C ₆ H ₅	4-OCF ₃	138-139
97	4-Cl	CH ₃	C ₆ H ₅	4-CF ₃	123-152
98	4-Cl	CH ₃	CO ₂ CH ₃	4-OCF ₃	126-127
99	4-Cl	H	C ₆ H ₅	4-OCF ₃	216-217

-(CH₂)₄-

Example	R	R ₁	R ₂	R ₄	mp °C
100	4-Cl	C ₆ H ₅	C ₆ H ₅	4-OCF ₃	122-123
101	4-Cl	H	CH ₂ C ₆ H ₅	4-OCF ₃	106-108
102	4-Cl	H	CH ₃	4-OCF ₃	116-118
103	4-Cl	-(CH ₂) ₃ -		4-CF ₃	167-168
104	4-Cl	H	CH ₃	4-CF ₃	132-133
105	4-Cl	H	C ₆ H ₅	4-CF ₃	208-210
106	4-Cl	-(CH ₂) ₃ -		4-OCF ₃	130-131
107	4-Cl	H	CH ₂ C ₆ H ₅	4-CF ₃	137-138
108	4-Cl	CH ₃	CO ₂ CH ₃	4-CF ₃	162-163
109	4-Cl	CH ₃	C ₂ H ₅	4-CF ₃	146-147
110	4-Cl	C ₂ H ₅	C ₂ H ₅	4-CF ₃	118-119
111	4-Cl	C ₂ H ₅	CH ₃	4-OCF ₃	119-120
112	4-Cl	C ₂ H ₅	C ₂ H ₅	4-OCF ₃	84-86
113	4-Cl	CH ₃	3-pyridyl	4-CF ₃	137-138
114	4-Cl	CH ₃	3-pyridyl	4-OCF ₃	66-67
115	4-Cl	CH ₃	4-Cl-C ₆ H ₄	4-CF ₃	219-220
116	4-Cl	CH ₃	4-Cl-C ₆ H ₄	4-OCF ₃	222-223
117	4-Cl	CH ₃		4-CF ₃	170-171
118	4-Cl	CH ₃		4-OCF ₃	141-142

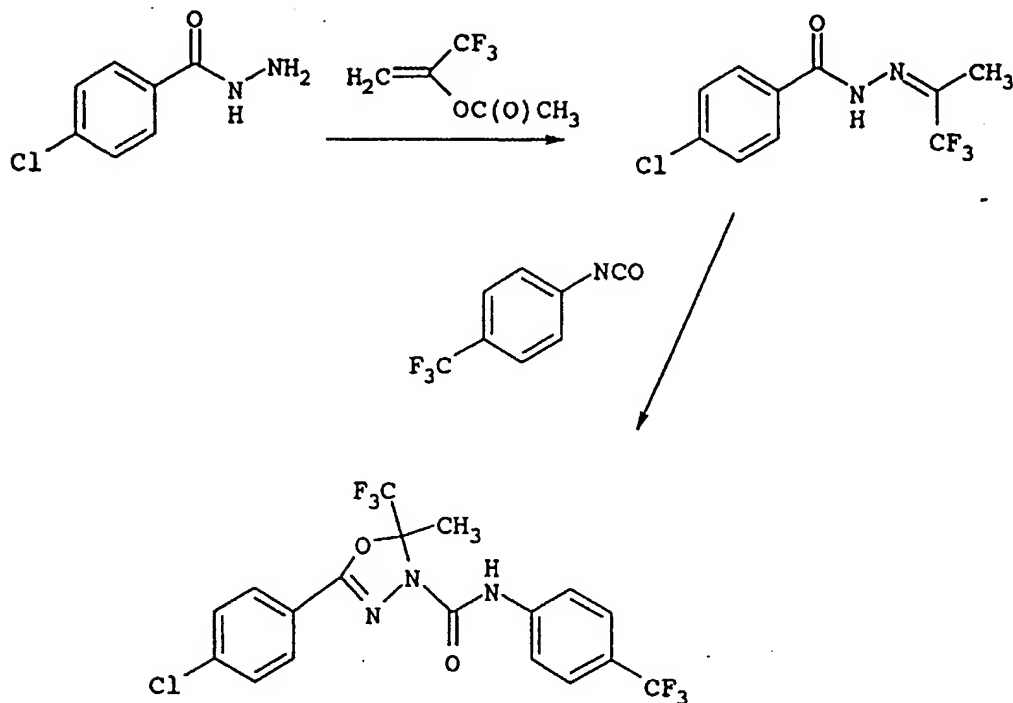
Example	R	R ₁	R ₂	R ₄	mp °C
119	4-Cl	1-indanylidene		4-CF ₃	76-77
120	4-Cl	CH ₃	CH ₂ Cl	4-CF ₃	183-184
121	4-Cl	CH ₃	CH ₂ Cl	4-OCF ₃	166-167
122	4-Cl	CH ₃	CH ₂ F	4-CF ₃	195-196
123	4-Cl	CH ₃	CH ₂ F	4-OCF ₃	176-177
124	4-Cl	CH ₂ Cl	CH ₂ Cl	4-CF ₃	197 (dec.)
125	4-Cl	CH ₃	CH ₂ CO ₂ CH ₃	4-CF ₃	145-147
126	4-Cl	CH ₃	CH ₂ CO ₂ CH ₃	4-OCF ₃	138-139
127	4-Cl	CH ₃	CH ₂ OC ₆ H ₅	4-CF ₃	128-129
128	4-Cl	CH ₃	CH ₂ OC ₆ H ₅	4-OCF ₃	100-101
129	4-F	CH ₃	CH ₂ Cl	4-CF ₃	143-144
130	4-Br	CH ₃	CH ₂ Cl	4-CF ₃	175-176
131	4-F	CH ₃	CH ₂ Cl	4-OCF ₃	101-103
132	4-Br	CH ₃	CH ₂ Cl	4-OCF ₃	155-156
133	4-Cl	CH ₃	CHCl ₂	4-CF ₃	175-176
134	4-Cl	CH ₃	CHCl ₂	4-OCF ₃	135-136
135	4-Cl	CH ₃	CH ₂ CF ₃	4-CF ₃	131-132
136	4-Cl	CH ₃	CH ₂ CF ₃	4-OCF ₃	106-107
137	4-Cl	CH ₃	CH ₂ OCH ₃	4-OCF ₃	112-113
138	4-Cl	CH ₃	CH ₂ OCH ₃	4-CF ₃	165-166

Example	R	R ₁	R ₂	R ₄	mp °C
139	4-Cl	CH ₃	CH ₂ OC(O)CH ₃	4-CF ₃	147-148
140	4-Cl	CH ₃	CH ₂ OC(O)CH ₃	4-OCF ₃	117-118
141	4-Cl	CH ₃	3-thienyl	4-OCF ₃	223
142	4-Cl	CH ₃	2-thiophene	4-CF ₃	196
143	4-Cl	CH ₃	2-furyl	4-CF ₃	172
144	4-Cl	CH ₃	3-thienyl	4-CF ₃	201
145	4-Cl	CH ₃	2-pyridyl	4-CF ₃	136
146	4-Cl	CH ₃	2-pyridyl	4-OCF ₃	135
147	4-Br	CH ₃	2-pyridyl	4-CF ₃	151-153
148	4-Br	CH ₃	2-pyridyl	4-OCF ₃	135-136
149	4-Cl	CH ₃	CH ₂ C ₆ H ₅	4-OCF ₃	125-126
150	4-Cl	CH ₃	CH ₂ -4-OCH ₃ - C ₆ H ₄	4-CF ₃	145
151	4-Cl	CH ₃	CH ₂ -4-OCH ₃ - C ₆ H ₄	4-OCF ₃	124
152	4-I	CH ₃	2-pyridyl	4-CF ₃	154
153	4-I	CH ₃	2-pyridyl	4-OCF ₃	151-152
154	4-Cl	CH ₃	4-F-C ₆ H ₄	4-CF ₃	202
155	4-Cl	CH ₃	4-OCH ₃ -C ₆ H ₄	4-CF ₃	168-170
156	4-Cl	CH ₃	CH ₂ C ₆ H ₅	4-CF ₃	130
157	4-Cl	CH ₃	4-F-C ₆ H ₄	4-OCF ₃	189-190
158	4-Cl	CH ₃	4-Br-C ₆ H ₄	4-OCF ₃	218-219

55

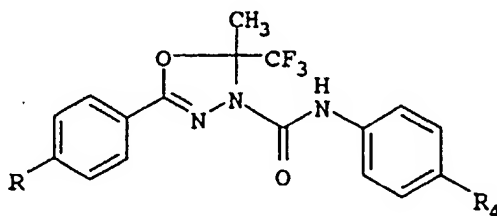
EXAMPLE 166**Preparation of 2-(*p*-Chlorophenyl)-5-methyl-5-trifluoromethyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide**

[0036]



[0037] A mixture of *p*-chlorobenzoyl hydrazine (1.77 g), 1-trifluoromethyl-1-acetoxyethylene (1.78 g) and ethanol (35 mL) is refluxed for 17 hours, cooled to room temperature, and concentrated *in vacuo* to obtain the corresponding benzoyl hydrazone (0.71 g). A mixture of the hydrazone (0.8 g) and 1,2-dichloroethane (10 mL) is treated with a *p*-trifluoromethylphenylisocyanate (0.67 g), heated at reflux for 87 hours, and concentrated *in vacuo* to obtain a colorless solid (1.48 g). Flash chromatography of the solid on silica gel (25% CH₂Cl₂/hexanes to 50% CH₂Cl₂/hexanes) gives the title product as a colorless solid (0.16 g, m.p. 157-158°C).

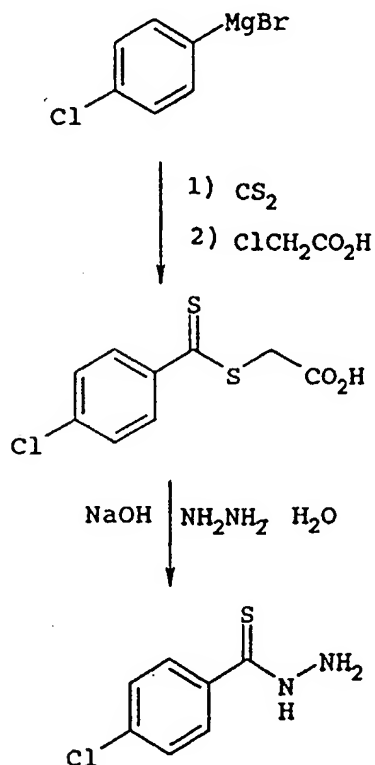
[0038] Using essentially the same procedure as described for Example 166, but using the appropriately substituted hydrazine and isocyanate, the following compounds are obtained.



Example	R	R ₄	mp °C
167	Cl	OCF ₃	128-129
168	Br	CF ₃	156-157
169	F	CF ₃	141-142

EXAMPLE 170**Preparation of *p*-chlorobenzoylthiohydrazide**

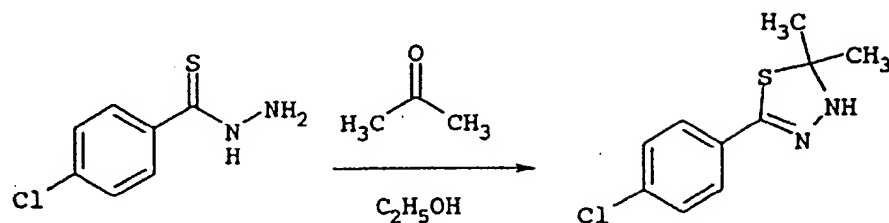
[0039]



[0040] A solution of carbon disulfide (4.5 mL, 75 mmol) and tetrahydrofuran (50 mL) is cooled to 0°C, treated dropwise with a solution *p*-chlorophenylmagnesium bromide (50 mL of 1M solution) at a rate that maintains the temperature below 10°C, warmed to and stirred at room temperature for 2 hours, concentrated *in vacuo* and diluted with water. The resultant aqueous mixture is filtered through diatomaceous earth. The filtrate is treated with a solution of chloroacetic acid (5.67 g), sodium hydrogen carbonate (3.82 g) and water (24 mL), stirred for three days at room temperature, acidified to pH 1 with 50% aqueous sulfuric acid and filtered to obtain the thioester (8.98 g). To a cold (0°C) solution of the thioester (3.5 g), sodium hydroxide (0.58 g) and water (35 mL) is added hydrazine hydrate (1.4 g). During the addition, the color changes from red to yellow and a solid precipitates. The solid is collected, washed with water, and dried to give the title product (1.92 g, m.p. 112-114°C).

EXAMPLE 171Preparation of 2-(p-chlorophenyl)-5,5-dimethyl- Δ^2 -1,3,4-thiadiazoline

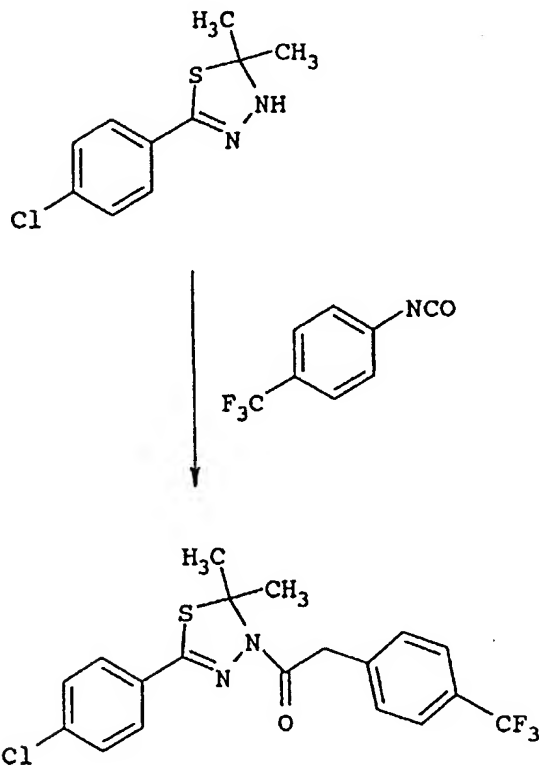
[0041]



[0042] A solution of p-chlorobenzoylthiohydrazine (1.02 g), acetone (1.89 g) and ethanol (5 mL) is stirred at room temperature for 4 days and the solvents are evaporated to obtain a brown solid. Flash chromatography of the brown solid on silica gel (10% ethyl acetate/hexanes) gives the title product as a yellow solid (0.44 g, m.p. 51-53°C).

EXAMPLE 172Preparation of 2-(p-Chlorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-thiadiazoline-4-carboxanilide

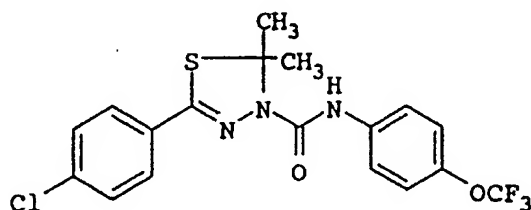
[0043]



[0044] A solution of 2-(p-chlorophenyl)-5,5-dimethyl- Δ^2 -1,3,4-thiadiazoline (0.33 g) and 1,2-dichloroethane (8 mL)

is treated with *p*-trifluoromethylphenylisocyanate (0.30 g), stirred for 72 hours at room temperature, and concentrated *in vacuo* to obtain a solid. Flash chromatography of the solid on silica gel (30% methylene chloride/hexanes) gives the title product as a colorless solid (0.61 g, m.p. 129-131°C).

[0045] Using essentially the same procedure as described for Example 172, but using the appropriately substituted isocyanate, the following compound is obtained:

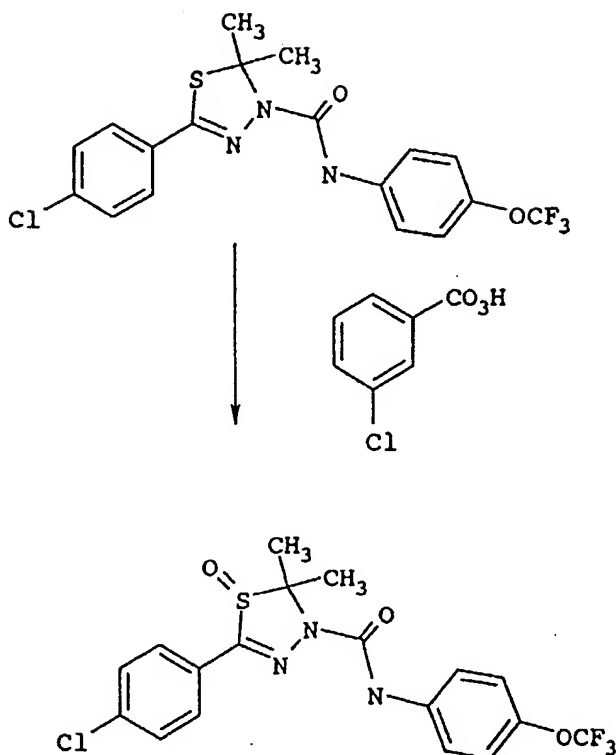


Example 173 mp 102-103°C

EXAMPLE 174

Preparation of 1-Oxide-2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-thiadiazoline-4-carboxanilide

[0046]



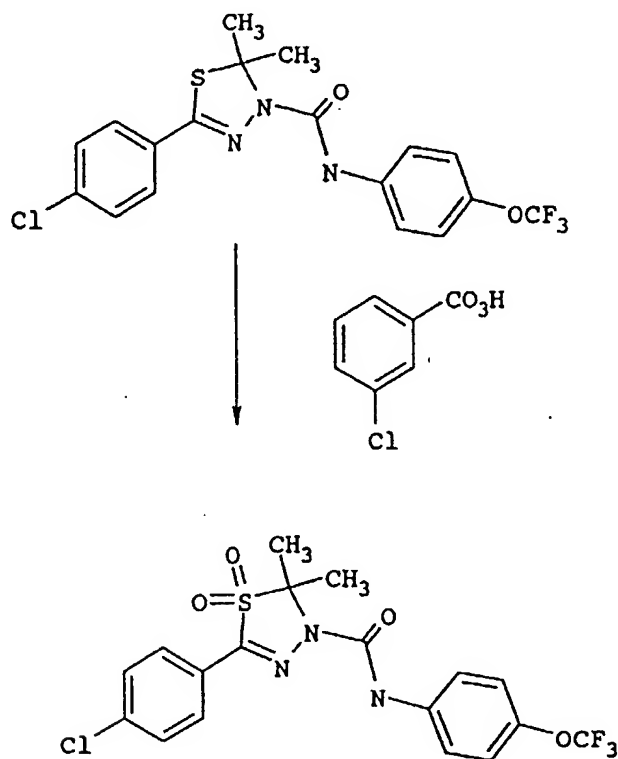
[0047] A solution of 2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-thiadiazoline-4-carboxanilide (0.50 g) and dichloromethane (15 mL) is stirred at -5° C, treated with 3-chloroperoxybenzoic acid (0.30 g, 70%), stirred

for 3.5 hours at room temperature, and diluted with dichloromethane (10 mL). The resultant mixture is washed with 5% sodium carbonate solution, dried over anhydrous magnesium sulfate, concentrated to 10 mL volume, and cooled in a refrigerator overnight. The white precipitate is filtered and dried to give the title product as a colorless solid (0.49 g, m.p. 214-215°C).

EXAMPLE 175

Preparation of 1,1-Dioxide-2-(p-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-thiadiazoline-4-carboxanilide

[0048]



[0049] A solution of 2-(p-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-thiadiazoline-4-carboxanilide (0.50 g) and dichloromethane (15 mL) is stirred at -5°C, treated with 3-chloroperoxybenzoic acid (1.79 g, 70%), stirred for 18 hours at room temperature, treated with additional 3-chloroperoxybenzoic acid (0.12 g, 70%), stirred for 14 hours at room temperature, washed with 5% sodium carbonate solution, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to obtain a solid. Flash chromatography of the solid on silica gel using a 10% ethyl acetate in hexanes solution gives the title product as a colorless solid (0.42 g, m.p. 181°C).

EXAMPLE 176

Insecticidal and acaricidal evaluation of test compounds

[0050] Test solutions are prepared by dissolving the test compound in a 35% acetone in water mixture to give a concentration of 10,000 ppm. Subsequent dilutions are made with water as needed.

Spodoptera eridania, 2nd instar larvae, southern armyworm (SAW)

[0051] A Sieva lima bean leaf expanded to 7-8 cm in length is dipped in the test solution with agitation for 3 seconds and allowed to dry in a hood. The leaf is then placed in a 100 x 10 mm petri dish containing a damp filter paper on the bottom and ten 2nd instar caterpillars. At 5 days, observations are made of mortality, reduced feeding, or any interference with normal molting.

Diabrotica virgifera virgifera Leconte, 2nd instar western corn rootworm (WCR)

[0052] One cc of fine talc is placed in a 30 mL wide-mouth screw-top glass jar. One mL of the appropriate acetone test solution is pipetted onto the talc so as to provide 1.25 mg of active ingredient per jar. The jars are set under a gentle air flow until the acetone is evaporated. The dried talc is loosened, 1 cc of millet seed is added to serve as food for the insects and 25 mL of moist soil is added to each jar. The jar is capped and the contents thoroughly mixed mechanically. Following this, ten 2nd instar rootworms are added to each jar and the jars are loosely capped to allow air exchange for the larvae. The treatments are held for 5 days when mortality counts are made. Missing larvae are presumed dead, since they decompose rapidly and cannot be found. The concentrations of active ingredient used in this test correspond approximately to 50 kg/ha.

Tetranychus urticae (OP-resistant strain), 2-spotted spider mite (TSM)

[0053] Sieva lima bean plants with primary leaves expanded to 7-8 cm are selected and cut back to one plant per pot. A small piece is cut from an infested leaf taken from the main colony and placed on each leaf of the test plants. This is done about 2 hours before treatment to allow the mites to move over to the test plant to lay eggs. The size of the cut, infested leaf is varied to obtain about 100 mites per leaf. At the time of test treatment, the piece of leaf used to transfer the mites is removed and discarded. The newly-infested plants are dipped in the test solution for 3 seconds with agitation and set in the hood to dry. After 2 days, one leaf is removed and mortality counts are made.

Aphis gossypii, cotton aphid (CA)

[0054] Cotton plants at the cotyledon stage are selected and cut back to one plant per pot. A heavily infested leaf is taken from the main colony and placed on top of each cotyledon. The aphids are allowed to transfer to the host plant overnight. At the time of test treatment, the leaf used to transfer the aphids is removed and discarded. The cotyledons are dipped in the test solution and allowed to dry. After 5 days, mortality counts are made.

Diabrotica undecimpunctata howardi, eggs-southern corn rootworm (SCR-Eggs)

[0055] Wells containing artificial diet are treated with the test solutions and dried. Southern corn rootworm eggs are then placed in the wells. The wells are covered with vented, adhesive, clear plastic covers. After 7 days, mortality counts are made.

Heliothis virescens, 3rd instar tobacco budworm (TBW)

[0056] Cotton cotyledons are dipped in the test solution and allowed to dry in a hood. When dry, each is cut into quarters and ten sections are placed individually in 30 mL plastic medicine cups containing a 5 to 7 mm long piece of damp dental wick. One 3rd instar caterpillar is added to each cup and a cardboard lid placed on the cup. Treatments are maintained for 3 days before mortality counts and estimates of reduction in feeding damage are made.

[0057] The tests are rated according to the scale shown below and the data obtained are shown in Table I.

Rating Scale	
0 = no effect	5 = 56-65% kill
1 = 10-25% kill	6 = 66-75% kill
2 = 26-35% kill	7 = 76-85% kill
3 = 36-45% kill	8 = 86-99% kill
4 = 46-55% kill	9 = 100% kill

TABLE I

Insecticidal and Acaricidal Evaluations						
Ex.	CA (300 ¹)	SAW (300 ¹)	TBW (300 ¹)	TSM (300 ¹)	SCR Eggs (1000 ¹)	WCR (50 ¹)
1	0	9	4	0	9	0
2		9	9	0	9	
3	0	9	9	0	9	4
4	0	4		0	0	0
5	0	9	3	2	9	0
6	0	9	9	0	9	1
7	0	9	8	0	9	0
8	0	0		0	0	00
9	0	9	9	0	9	2
10	0	9	3	0	9	0
11	0	0		9	0	0
12	0	9	9	0	9	0
13	0	7	0	0	0	0
14	0	9	9	0	9	0
15	0	0		4	0	0
16	0	8	0	0	9	0
17	0	9	0	0	0	0
18	0	0		0	0	1
19					0	
20					0	
21					0	
22	0	1		0	0	0
23	0	8	0	0	0	1
24	0	2		0	0	0
25	0	2		3	0	0
26	0	0		0	0	1
27	0	9	9	0	9	0
28	0	9	9	0	9	4
29	0	9	0	0	9	0
30	0	9	1	0	9	0
31	0	9	0	0	9	0
32	0	9	8	0	9	0
33	0	9	1	0	9	0
34	0	9	9	0	9	0
35	0	9	9	0	9	0
36	5	9	8	0	9	9
37	0	9	0	0	9	0
38	0	9	1	0	8	0
39	0	9	1	0	9	1
40	0	9	3	0	9	0
41	0	9	3	0	9	0
42	0	1		0	9	0
43	0	9	9	0	9	0
44	0	9	0	0	9	0
45	0	8	0	0	0	0

¹ rates in ppm

EP 1 004 241 A1

TABLE I (continued)

Insecticidal and Acaricidal Evaluations						
Ex.	CA (300 ¹)	SAW (300 ¹)	TBW (300 ¹)	TSM (300 ¹)	SCR Eggs (1000 ¹)	WCR (50 ¹)
46	0	8	0	0	0	0
47	0	9	5	0	0	0
48	0	9	6	0	9	0
49	0	9	1	0	9	7
50	0	9	0	0	0	0
51	0	9	5	0	0	0
52	0	9	0	0	0	0
53	0	9	0	0	9	4
54	0			0	0	4
55	0			0	8	0
56	0			0	8	0
57	8	0		0	7	0
58	0	8	0	0	0	0
59	0	9	9	0	9	0
60	0	9	9	0	9	0
61	0	9	0	0	9	0
62	0	9	1	0	0	0
63	0	9	0	0	9	0
64	0	9	9	0	9	0
65	0	9	7	0	9	0
66	0	4		0	0	0
67	0	9	9	0	9	0
68	0	8	1	0	8	9
69	0	9	9	0	9	2
70	0	3		0	0	1
71	0	1		0	0	3
72	0	1		0	0	2
73		6		0	9	2
74	0	9	6	0	7	1
75	0	1		0	7	9
76	0	0		0	0	4
77	0	9	0	0	8	0
78	0	9	0	0	8	0
79	0	9	0	0	9	1
80	0	3		0	0	9
81	0	1		0	0	0
82	0	6		0	0	2
83	0	3		0	0	0
84	0	0		0	0	0
85	0	0		0	0	3
86	0	9	9	0		4
87	0	9	8	0		9
88	0	9	0	0		0
89	0	9	1	0		0
90	0	8	0	0		0
91	0	9	7	0		0

¹ rates in ppm

EP 1 004 241 A1

TABLE I (continued)

Insecticidal and Acaricidal Evaluations						
Ex.	CA (300 ¹)	SAW (300 ¹)	TBW (300 ¹)	TSM (300 ¹)	SCR Eggs (1000 ¹)	WCR (50 ¹)
5	92	0	9	0	0	0
	93	0	9	0	0	0
	94	0	9	7	0	0
10	95	0	9	9	0	9
	96	0	0	0	0	0
	97	0	9	3	0	9
	98	0	9	3	0	9
	99	0	9	0	0	0
15	100	0	0	0	0	0
	101	0	9	8	0	9
	102	0	9	6	0	7
	103	0	9	9	0	8
20	104	0	9	2	0	8
	105	0	9	3	0	0
	106	0	9	1	0	9
	107	0	9	2	0	9
	108	0	0	0	0	4
25	109	0	9	8	0	9
	110	0	9	7	0	9
	111	0	9	9	4	9
	112	0	9	9	0	9
30	113	0	9	4	0	9
	114	0	9	2	0	9
	115	0	9	9	0	9
	116	0	9	9	0	8
	117	0	9	7	0	8
35	118	0	7	0	0	8
	119	0	8	9	0	0
	120	0	9	9	0	9
	121	0	9	9	0	9
40	122	0	9	8	0	0
	123	0	9	9	0	0
	124	0	5	0	0	0
	125	0	9	7	0	8
	126	0	9	0	0	9
45	127	0	9	6	0	8
	128	0	9	6	0	9
	129	0	9	9	0	2
	130	0	9	9	0	0
50	131	0	9	9	0	0
	132	0	9	9	0	0
	133	0	9	8	0	0
	134	7	9	6	2	1
	135	0	9	0	0	1
55	136	0	9	0	0	2
	137	0	9	3	0	0

¹ rates in ppm

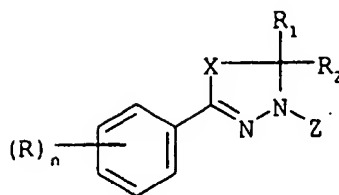
TABLE I (continued)

Insecticidal and Acaricidal Evaluations						
Ex.	CA (300 ¹)	SAW (300 ¹)	TBW (300 ¹)	TSM (300 ¹)	SCR Eggs (1000 ¹)	WCR (50 ¹)
138	0	6		0		9
139	0	8		0		2
140	0	9		0		3
141	0	8	0	0	9	0
142	0	2		0	0	1
143	0	0		0	0	0
144	0	2		0	9	2
145	0	9	0	0	0	6
146	0	9	8	0	9	0
147	0	9		0	0	6
148	0	6		0	0	7
149	0	9		0	9	0
150	0	0		0	0	0
151	0	0		0	9	0
152	0	4	0	0	9	0
153	0	0		0	0	0
154	0	9	4	0	8	0
155	0	9	0	0	9	0
156	0	0		0	9	0
157	0	9	9	0	9	4
158	0	8	0	0	9	0
159	0	9	9	0	9	0
160	0	4		0	9	3
161	0	9	7	0	0	0
162	0	9	9	0	8	0
163	0	6		0	8	0
164	0	9	7	0		3
165	0	9		0		8
166	0	9	9	0	9	0
167	0	9	9	0	7	4
168	0	9	9	0	9	0
169	0	9	9	0	9	0
172	0	9	9	0		0
173	0	9	9	0		0

¹ rates in ppm

Claims

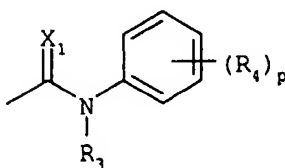
1. A method for the control of insect or acarid pests which comprises contacting said pests or their food supply, habitat or breeding grounds with a pesticidally effective amount of a compound having the structural formula



wherein

X is O or S(O)_m;

Z is

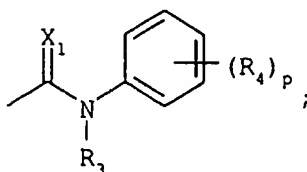


C(X₁)R₅, C₁-C₆alkyl, C₁-C₆haloalkyl,

benzyl optionally substituted on the phenyl ring with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, or

phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups,

provided that when X is O, Z is



n and p are each independently 0, 1, 2 or 3;

X₁ is O or S;

R and R₄ are each independently halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, OR₆, S(O)_qR₇, nitro, cyano, NR₈R₉, CO₂R₁₀, C(O)R₁₁ or

phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, or two adjacent R groups or R₄ groups may be taken together to form a ring wherein RR or R₄R₄ is represented by: -OCH₂O-, -OCF₂O- or -CH=CH-CH=CH-; R₆ and R₇ are each independently hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or

phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups;

R₈, R₉, R₁₃ and R₁₄ are each independently hydrogen, C₁-C₆alkyl, C₁-C₆alkylcarbonyl or

phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups;

R₁₀ and R₁₁ are each independently hydrogen, C₁-C₆alkyl or C₁-C₆haloalkyl;

R₁ and R₂ are each independently hydrogen, C₃-C₇cycloalkyl, C₁-C₆haloalkyl, C₃-C₆alkenyl, C₃-C₆haloalkenyl, C₃-C₆alkynyl, C₃-C₆haloalkynyl, C₂-C₆alkoxyalkyl, (CH₂)_vC(O)R₁₂,

C₁-C₆alkyl optionally substituted with one phenoxy or phenyl group wherein the phenyl ring of each group is independently, optionally substituted with from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, phenyl optionally substituted with from one to

three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, or

a 5- or 6-membered heteroaromatic ring optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, and

when R₁ and R₂ are taken together with the atom to which they are attached they may form a C₃-C₆cycloalkyl ring wherein R₁R₂ is represented by: -(CH₂)_t, where t is 2, 3, 4 or 5;

m, q and v are each independently 0, 1 or 2;

R₁₂ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio, C₁-C₆haloalkylthio or NR₁₃R₁₄;

R₃ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or C(O)R₁₅;

R₁₅ is C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy or C₁-C₆haloalkoxy; and

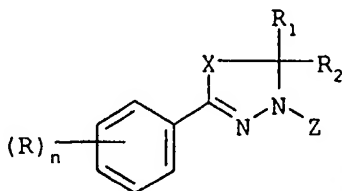
R₅ is C₁-C₆alkyl,

phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, or benzyl optionally substituted on the phenyl ring with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups; and the optical isomers thereof and the agriculturally acceptable salts thereof.

2. The method according to claim 1 wherein the compound is selected from the group consisting of

2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-bromophenyl)-5,5-dimethyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-fluorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 5,5-dimethyl-2-(*p*-phenoxyphenyl)-4'-[(trifluoromethyl)-thio]-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-4'-(trifluoromethoxy)-5-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-chlorophenyl)-5-methyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 4,5-bis(trifluoromethyl)-2-(*p*-fluorophenyl)-5-methyl-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-fluorophenyl)-5-methyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-fluorophenyl)-5-methyl-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-bromophenyl)-5-(chloromethyl)-5-methyl-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;
 methyl N-[[2-(*p*-chlorophenyl)-5,5-dimethyl-Δ²-1,3,4-oxadiazolin-4-yl]carbonyl]-*p*-(trifluoromethoxy)-carbanilate;
 methyl N-[[2-(*p*-chlorophenyl)-5,5-dimethyl-Δ²-1,3,4-oxadiazolin-4-yl]carbonyl]-*p*-(trifluoromethyl)-carbanilate; and
 methyl 2-(*p*-chlorophenyl)-5-methyl-4-[[*p*-(trifluoromethoxy)phenyl]carbonyl]-Δ²-1,3,4-oxadiazoline-5-acetate.

3. A method for the protection of growing plants from attack or infestation by insect or acarid pests which comprises applying to the foliage of the plants, or to the soil or water in which they are growing, a pesticidally effective amount of a compound having the structural formula



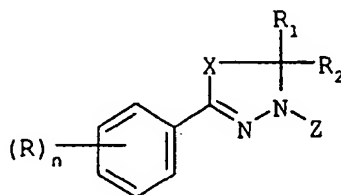
wherein n, R, R₁, R₂, X and Z are as described in claim 1.

4. The method according to claim 3 wherein the compound is selected from the group consisting of

2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-bromophenyl)-5,5-dimethyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-fluorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 5,5-dimethyl-2-(*p*-phenoxyphenyl)-4'-[(trifluoromethyl)-thio]- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-4'-(trifluoromethoxy)-5-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-chlorophenyl)-5-methyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 4,5-bis(trifluoromethyl)-2-(*p*-fluorophenyl)-5-methyl- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-fluorophenyl)-5-methyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-fluorophenyl)-5-methyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-bromophenyl)-5-(chloromethyl)-5-methyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 methyl N-[[2-(*p*-chlorophenyl)-5,5-dimethyl- Δ^2 -1,3,4-oxadiazolin-4-yl]carbonyl]-*p*-(trifluoromethoxy)-carbanilate;
 methyl N-[[2-(*p*-chlorophenyl)-5,5-dimethyl- Δ^2 -1,3,4-oxadiazolin-4-yl]carbonyl]-*p*-(trifluoromethyl)-carbanilate; and
 methyl 2-(*p*-chlorophenyl)-5-methyl-4'-[[*p*-(trifluoromethoxy)phenyl]carbamoyl]- Δ^2 -1,3,4-oxadiazoline-5-acetate.

5. The method according to claim 3 wherein the compound is applied to the plants, or to the soil or water in which they are growing, at a rate of about 0.1 kg/ha to 4.0 kg/ha.

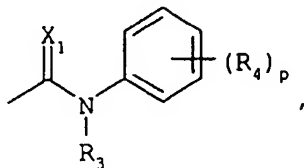
6. A compound having the structural formula



wherein

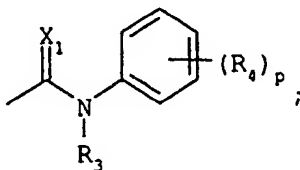
X is O or S(O)_m;

Z is



C(X₁)R₅, C₁-C₆alkyl, C₁-C₆haloalkyl,

benzyl optionally substituted on the phenyl ring with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, or phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, provided that when X is O, Z is



n and p are each independently 0, 1, 2 or 3;

X₁ is O or S;

R and R₄ are each independently halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, OR₆, S(O)_qR₇, nitro, cyano, NR₈R₉, CO₂R₁₀, C(O)R₁₁ or

phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, or two adjacent R groups or R₄ groups may be taken together to form a ring wherein RR or R₄R₄ is represented by: -OCH₂O-, -OCF₂O- or -CH=CH-CH=CH-;

R₆ and R₇ are each independently hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or

phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups;

R₈, R₉, R₁₃ and R₁₄ are each independently hydrogen, C₁-C₆alkyl, C₁-C₆alkylcarbonyl or

phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups;

R₁₀ and R₁₁ are each independently hydrogen, C₁-C₆alkyl or C₁-C₆haloalkyl;

R₁ and R₂ are each independently hydrogen, C₃-C₇cycloalkyl, C₁-C₆haloalkyl, C₃-C₆alkenyl, C₃-C₆haloalkenyl, C₃-C₆alkynyl, C₃-C₆haloalkynyl, C₂-C₆alkoxyalkyl, (CH₂)_vC(O)R₁₂, C₁-C₆alkyl optionally substituted with one phenoxy or phenyl group wherein the phenyl ring of each group is independently, optionally substituted with from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, phenyl optionally substituted with from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, or

a 5- or 6-membered heteroaromatic ring optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, and

when R₁ and R₂ are taken together with the atom to which they are attached they may form a C₃-C₆cycloalkyl ring wherein R₁R₂ is represented by: -(CH₂)_t-where t is 2, 3, 4 or 5;

m, q and v are each independently 0, 1 or 2;

R₁₂ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio, C₁-C₆haloalkylthio or NR₁₃R₁₄;

R₃ is hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or C(O)R₁₅;

R₁₅ is C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy or C₁-C₆haloalkoxy; and

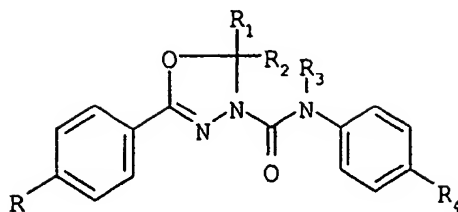
R₅ is C₁-C₆alkyl,

phenyl optionally substituted with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups, or benzyl optionally substituted on the phenyl ring with any combination of from one to three halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₁-C₆alkylthio or C₁-C₆haloalkylthio groups; and

the optical isomers thereof and the agriculturally acceptable salts thereof,

provided that: (1) R is other than CO₂R₁₀ when R is on the ortho-position of the phenyl ring, and (2) R₂ is other than ethyl or unsubstituted phenyl when X is O, n and p are 0 and R₁ is methyl.

7. The compound according to claim 6 having the structural formula



wherein

R is halogen, C₁-C₄haloalkyl, C₁-C₄haloalkoxy or

phenoxy optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups;

R₄ is C₁-C₄haloalkyl, C₁-C₄haloalkoxy or C₁-C₄haloalkylthio;

R₁ is C₁-C₄alkyl;

R₂ is C₁-C₄alkyl, C₁-C₄haloalkyl, (CH₂)_vC(O)R₁₂ or 2-pyridyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups;

v is 0 or 1;

R₁₂ is C₁-C₄alkoxy or C₁-C₄haloalkoxy;

R₃ is hydrogen or C(O)R₁₅; and

R₁₅ is C₁-C₄alkoxy.

8. The compound according to claim 6 selected from the group consisting of

2-(p-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

2-(p-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

2-(p-bromophenyl)-5,5-dimethyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

2-(p-fluorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

5,5-dimethyl-2-(p-phenoxyphenyl)-4'-[(trifluoromethyl)-thio]-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

2-(p-chlorophenyl)-5-methyl-4'-(trifluoromethoxy)-5-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

5-(chloromethyl)-2-(p-chlorophenyl)-5-methyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

4,5-bis(trifluoromethyl)-2-(p-fluorophenyl)-5-methyl-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

5-(chloromethyl)-2-(p-fluorophenyl)-5-methyl-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

5-(chloromethyl)-2-(p-fluorophenyl)-5-methyl-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

2-(p-bromophenyl)-5-(chloromethyl)-5-methyl-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

2-(p-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

2-(p-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

2-(p-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethyl)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

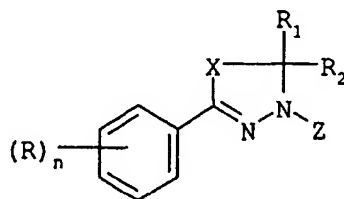
2-(p-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethoxy)-Δ²-1,3,4-oxadiazoline-4-carboxanilide;

methyl N-[[2-(p-chlorophenyl)-5,5-dimethyl-Δ²-1,3,4-oxadiazolin-4-yl]carbonyl]-p-(trifluoromethoxy)-carbanilate;

methyl N-[[2-(p-chlorophenyl)-5,5-dimethyl-Δ²-1,3,4-oxadiazolin-4-yl]carbonyl]-p-(trifluoromethyl)-carbanilate; and

methyl 2-(p-chlorophenyl)-5-methyl-4'-[[p-(trifluoromethoxy)phenyl]carbamoyl]-Δ²-1,3,4-oxadiazoline-5-acetate.

9. A composition for the control of insect or acarid pests which comprises an agronomically acceptable carrier and a pesticidally effective amount of a compound having the structural formula



wherein n , R , R_1 , R_2 , X and Z are as described in claim 6.

10. The composition according to claim 9 wherein the compound is selected from the group consisting of

2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-bromophenyl)-5,5-dimethyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-fluorophenyl)-5,5-dimethyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 5,5-dimethyl-2-(*p*-phenoxyphenyl)-4'-(trifluoromethyl)-thio- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-4'-(trifluoromethoxy)-5-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-chlorophenyl)-5-methyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 4,5-bis(trifluoromethyl)-2-(*p*-fluorophenyl)-5-methyl- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-fluorophenyl)-5-methyl-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 5-(chloromethyl)-2-(*p*-fluorophenyl)-5-methyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-bromophenyl)-5-(chloromethyl)-5-methyl-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2,2,2-trifluoroethyl)-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethyl)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 2-(*p*-chlorophenyl)-5-methyl-5-(2-pyridyl)-4'-(trifluoromethoxy)- Δ^2 -1,3,4-oxadiazoline-4-carboxanilide;
 methyl N-[[2-(*p*-chlorophenyl)-5,5-dimethyl- Δ^2 -1,3,4-oxadiazolin-4-yl]carbonyl]-*p*-(trifluoromethoxy)-carbanilate;
 methyl N-[[2-(*p*-chlorophenyl)-5,5-dimethyl- Δ^2 -1,3,4-oxadiazolin-4-yl]carbonyl]-*p*-(trifluoromethyl)-carbanilate; and
 methyl 2-(*p*-chlorophenyl)-5-methyl-4-[[*p*-(trifluoromethoxy)phenyl]carbonyl]- Δ^2 -1,3,4-oxadiazoline-5-acetate.



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 99 30 9154 shall be considered, for the purposes of subsequent proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131018 Beilstein Registry Number 5026402 & J. CHEM. SOC. PERKIN TRANS. 1, 1986, pages 1499-1506, ---	6	A01N47/38 A01N43/824 C07D271/10 C07D271/12 C07D413/04 C07D417/04
X	DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131019 Beilstein Registry Number 7112673 & J. CHEM. SOC. PERKIN TRANS. 1, no. 9, 1982, pages 1993-1998, --- -/--	6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			A01N C07D
INCOMPLETE SEARCH			
<p>The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.</p> <p>Claims searched completely :</p> <p>Claims searched incompletely :</p> <p>Claims not searched :</p> <p>Reason for the limitation of the search:</p> <p>see sheet C</p>			
Place of search		Date of completion of the search	Examiner
THE HAGUE		21 February 2000	ALLARD, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EP 99 30 9154 (P44007)



European Patent
Office

INCOMPLETE SEARCH
SHEET C

Application Number
EP 99 30 9154

Reason for the limitation of the search:

Present claim 6 lacks novelty within the meaning of Article 54 EPC to such an extent that neither a complete search nor a complete search report are possible with regard to this claim. The cited documents should only be considered as a representative selection from the prior art.



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

EP 99 30 9154

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131020 Beilstein Registry Number 4997767 & J. ORG. CHEM. USSR, vol. 20, 1984, pages 152-162, ---	6	
X	DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131021 Beilstein Registry Number 270154 & J. PHARM. CHIM., vol. 8, no. 22, 1935, page 289, 296 ---	6	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131022 Beilstein Registry Number 199485 & ARK. KEMI, vol. 9, 1956, page 47, 57 ---	6	
X	DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131023 Beilstein Registry Number 1010910 & ACTA CHEM. SCAND., vol. 14, 1960, pages 789-796, --- -/--	6	

EPO FORM 1503 03.82 (P04C10)



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 99 30 9154

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<p>DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131024 Beilstein Registry Number 546209 & ARG. MASS SPECTROM., vol. 9, 1974, page 181, 182</p> <p>---</p>	6	
X	<p>DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131025 Beilstein Registry Number 204553 & BULL. SOC. CHIM. BELG., vol. 46, 1937, page 231, 239</p> <p>---</p>	6	<p>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</p>
X	<p>DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131026 Beilstein Registry Number 234971 and 244463 & BULL. SOC. CHIM. BELG., vol. 43, 1934, page 206, 207, 208, 209</p> <p>---</p>	6	
X	<p>DATABASE CROSSFIRE Beilstein Institut für Literatur der organischen Chemie XP002131027 Beilstein Registry Number 36883, 186285 and 223472 & BULL. SOC. CHIM. BELG., vol. 43, 1934, page 261, 267</p> <p>---</p> <p style="text-align: center;">-/--</p>	6	

EPO FORM 1503 03.82 (P04C10)



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

EP 99 30 9154

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	US 4 140 787 A (SIRRENBURG W ET AL) 20 February 1979 * the whole document *	1	
A	GB 2 258 462 A (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V.) 10 February 1993 * the whole document *	1	
A	CHEMICAL ABSTRACTS, vol. 117, no. 11, 14 September 1992 Columbus, Ohio, US; abstract no. 111534f, SHABAN M A E ET AL: "Synthesis and biological activities of some 1,3,4-oxadiazoles and bis(1,3,4-oxadiazoles)" page 859; XP002131017 * abstract * & ALEXANDRIA J. PHARM. SCI., vol. 6, no. 1, 1992, pages 17-21, -----	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7)

EPO FORM 1503 03.82 (P4C10)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 9154

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-02-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4140787 A	20-02-1979	DE 2700288 A	13-07-1978
		AT 356130 B	10-04-1980
		AT 9478 A	15-09-1979
		AT 363727 B	25-08-1981
		AT 344079 A	15-01-1981
		AU 517609 B	13-08-1981
		AU 3216278 A	12-07-1979
		BE 862662 A	05-07-1978
		BR 7800049 A	15-08-1978
		CA 1120044 A	16-03-1982
		CH 634304 A	31-01-1983
		CS 194830 B	31-12-1979
		DD 134038 A	07-02-1979
		DK 3378 A	06-07-1978
		ES 465759 A	16-09-1978
		FR 2376848 A	04-08-1978
		GB 1591280 A	17-06-1981
		GB 1591279 A	17-06-1981
		HU 177941 B	28-02-1982
		IL 53739 A	13-09-1981
		IT 1092954 B	12-07-1985
		JP 1306993 C	13-03-1986
		JP 53084970 A	26-07-1978
		JP 60033390 B	02-08-1985
		NL 7800039 A	07-07-1978
		NZ 186095 A	28-03-1979
		PL 203797 A	11-09-1978
		TR 19578 A	01-07-1979
		ZA 7800039 A	29-11-1978
GB 2258462 A	10-02-1993	NONE	

EPC FORM POUSS

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82